

## PATENT SPECIFICATION



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427,339

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Complete Specification Accepted: April 23, 1935.

(Under this Application, which was originally made under Section 91 of the Patents and Designs Acts, 1907 to 1932, a Specification was laid open to public inspection on April 30, 1934.)

## COMPLETE SPECIFICATION

## Improvements in or relating to Titanium Compounds

We, TITAN Co. A/S, of Fredriksstad, Norway, a Corporation organised and existing under and by virtue of the laws of the Kingdom of Norway, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 This invention is for improvements in or relating to the manufacture of titanium compounds, such as titanium dioxide, and pigments composed thereof, and consists in a modification of our  
15 British Patent No. 392,194 which relates to the addition of acid-binding substances to acid-poor solutions of titanium from which the titanium is hydrolytically precipitated.

20 The present invention comprises a process for the hydrolytic precipitation of titanium compounds from a solution containing titanium including the step which consists in adding an organic acid-binding substance to the titanium solution before or during hydrolysis, to  
25 initiate or maintain the hydrolysis.

The invention also includes a process for the manufacture of titanium compounds by hydrolysing an acid-poor  
30 titanium solution which contains a high concentration of titanium and which may contain bases other than titanium, wherein the titanium solution is first formed so that it contains an amount of acid sufficient for the formation of normal salts of the bases other than titanium and in addition a further amount of acid equal to or  
35 less than the amount required for the formation of the normal titanium salt (reckoned, for example, when sulphuric acid is used, as  $\text{Ti}(\text{SO}_4)_2$ ) and then hydrolysis is initiated or maintained in said solution by adding to the solution organic  
40 acid-binding substances in quantities which do not cause any considerable decrease in the total acidity of the solution. The organic acid-binding substance preferably comprises an organic base capable  
45 of liberating ammonia in acid solutions, for example, hexamethylenetetramine, acetamide or acetaldehyde ammonia.

[Price 1/-]

The titanium solution may be prepared by treating ilmenite with sulphuric acid and mixing the resulting sulphate mass  
55 with water to form a titanium sulphate solution from which the hydrated titanium oxide may be then hydrolytically precipitated by elevating the temperature of the solution to or near the  
60 boiling point. In carrying out the present invention it is found that the addition of organic bases before hydrolysis affects the hydrolytic decomposition reaction in such a manner that the precipitate obtained on calcination gives a product with excellent pigmental properties.

It has been found that organic bases such as hexamethylenetetramine  
( $\text{C}_6\text{H}_{12}\text{N}_4$ ), acetaldehyde ammonia  
( $\text{C}_2\text{H}_5\text{ON}$ ) and acetamide ( $\text{C}_2\text{H}_5\text{ON}$ )  
70 which liberate ammonia by decomposition in acid solutions are particularly effective in the process according to the invention. It is preferred to add these  
75 bases a short time before the precipitation of the titanium solution and at an elevated temperature.

For the production of a pigment the precipitate obtained is washed and calcined with or without addition of  
80 neutralising agents prior to calcination. The calcination may be carried out in the presence of sintering agents or compounds of phosphorus (phosphoric acid or phosphates) or both.

The improved process may with advantage be used in the preparation of composite titanium pigments, hydrolysis  
85 being carried out, according to known practice, in the presence of extenders (e.g. a sulphate of an alkaline earth metal) suspended in the titanium solution so that the titanium compounds are precipitated thereon. The composite  
90 precipitate is then washed and calcined and treated in the same manner as a precipitate consisting of titanium compounds only.

The following examples illustrate, by way of example only, several ways in which the process may be carried out.

## EXAMPLE I.

To 219 kgs. of a titanium ore solution

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of the following composition:—

13.7% . . . . .  $\text{TiO}_2$   
4.6% . . . . .  $\text{FeO}$   
21.6% . . . . . Titratable sul-  
phuric acid, and

2 grams per litre of  $\text{TiO}_2$  as titanous sulphate, is added at  $85^\circ \text{C}$ ., 230 grams of hexamethylenetetramine during 15 minutes. After standing for 15 minutes the solution is heated rapidly to the boiling point, and then maintained at an active boil for four hours. The precipitated hydrated titanium oxide is separated, washed and dried. The dried material is then calcined for four hours at  $875^\circ \text{C}$ . to form the substantially pure titanium oxide pigment.

#### EXAMPLE II.

To 219 kgs. of a titanium ore solution containing 13.7%  $\text{TiO}_2$ , 4.6%  $\text{FeO}$ , 21.6% titratable sulphuric acid, and 2 grams per litre of  $\text{TiO}_2$  as titanous sulphate, is added at  $85^\circ \text{C}$ ., 310 grams of acetaldehyde ammonia during 15 minutes. After standing 15 minutes the solution is heated rapidly to the boiling point, and then maintained at an active boil for four hours. The precipitated hydrated titanium oxide is separated, washed and dried. The dried material is then calcined for four hours at  $875^\circ \text{C}$ . with or without the addition of salts, such as sodium sulphate, which facilitate the crystallisation or improve the colour of the final pigment.

#### EXAMPLE III.

To 326 kgs. of a titanium ore solution containing 15.3%  $\text{TiO}_2$ , 4.5%  $\text{FeO}$ , 22.8% titratable sulphuric acid, and 2 grams per litre of  $\text{TiO}_2$  as titanous sulphate are added at  $85^\circ \text{C}$ ., 500 grams of acetamide during 15 minutes. After standing 15 minutes the solution is heated rapidly to the boiling point, and then maintained at an active boil for four hours. The precipitated hydrated titanium oxide is separated, washed and dried. The dried material is then calcined for four hours at  $875^\circ \text{C}$ .

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to

be performed, we declare that what we claim is:—

1. In the hydrolytic precipitation of titanium compounds from a solution containing titanium, the step which consists in adding an organic acid-binding substance to said solution before or during hydrolysis to initiate or maintain the hydrolysis.

2. A process for the manufacture of titanium compounds by hydrolysing an acid-poor titanium solution which contains a high concentration of titanium and which may contain bases other than titanium, wherein the titanium solution is first formed so that it contains an amount of acid sufficient for the formation of normal salts of the bases other than titanium and in addition a further amount of acid equal to or less than the amount required for the formation of the normal titanium salt (reckoned, for example, when sulphuric acid is used, as  $\text{Ti}(\text{SO}_4)_2$ ) and then hydrolysis is initiated or maintained in said solution by adding to the solution organic acid-binding substances in quantities which do not cause any considerable decrease in the total acidity of the solution.

3. A process as claimed in Claim 1 or Claim 2, wherein the acid-binding substance is an organic base capable of liberating ammonia such as hexamethylenetetramine or acetamide or acetaldehyde ammonia.

4. A process for the hydrolytic precipitation of titanium compounds from a sulphuric acid solution containing titanium, carried out substantially in accordance with any of the Examples I—III hereinbefore described.

5. A titanium pigment with or without an extender wherein the titanium compound is prepared in accordance with the process claimed in any of the preceding claims.

Dated this 23rd day of October, 1933.

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